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In situ x-ray characterization of the electrolyte-solid interface

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Electrochemically controlled surfaces are expected to be very different from those in vacuum due to high electric fields at the electrolyte-metal interface. Microscopic knowledge of that interface is essential in understanding technologically important processes like corrosion and electroplating. Underpotentially-deposited (UPD) layers of one metal on another are relatively stable, prototypical systems for such research. The Cu atomic-scale environment in a layer of Cu deposited electrochemically on a large polycrystalline Pt electrode has been studied *in situ* using both fluorescence-detection x-ray absorption spectroscopy (XAS) and measurements of x-ray reflectivity. Measurements were made on the same layer with the x-ray electric field vector both parallel and perpendicular to the surface normal vector, essential for the determination of the number of neighboring atoms. After a substantial effort in XAS experimental design and technique development, we have obtained significantly higher quality data than others. Moreover, we have achieved a consistent interpretation for these spectra, involving O, Cu, and Pt atoms as near neighbors. Their distances from Cu are identical in the two polarizations, but their amplitudes are different. These differences provide geometrical constraints on models proposed for the structure of the interface.

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1. Introduction

Many technologically important chemical processes occur at the liquid/solid interface, including corrosion and electroplating. While our current understanding of such processes is largely phenomenological, the need to develop more predictive models is widely recognized. There has been a steady growth in the number of researchers trying to obtain the detailed data required to develop accurate microscopic models.

The controlled ultra-thin metal layers produced through underpotential deposition (UPD) are a good starting point for such research. UPD layers have been observed in the electrodeposition of many metals onto unlike metal substrates, including Cu, Ag, Pb, or Tl onto Ag, Pt, or Au. They arise because the adsorbate metal atoms are bound more tightly to the unlike metal substrate than to like atoms. This allows the stabilization of an ultra-thin layer of adsorbate atoms on the substrate when the cathode (substrate) is held at a potential ~ 0.1 V more positive than that required for bulk deposition. Foreign metal overlayers containing anywhere from a fraction of a monolayer to two monolayers' worth of adsorbate atoms have been stabilized for hours under electrochemical control, each distinct state corresponding to a particular narrow range of applied potentials. Such a relatively stable system facilitates the accurate measurements needed to develop a detailed understanding. Furthermore, its stability enhances the likelihood that data developed under somewhat different circumstances or by different research groups will correspond to the same state of the system. This is particularly important in a field in which significantly more precise knowledge is being sought, which requires more careful identification and control of the crucial materials parameters.

UPD layers have been characterized extensively using standard electrochemical techniques. For example, charge transfer during layer growth and stripping can be measured using cyclic voltammetry. The application of techniques which yield *microscopic* information has, however, happened only recently.

Measurements of microscopic quantities generally involve direct or indirect probing of the *structure* of the electrolyte/layer/substrate interfacial region. Accurate and detailed structural information will be a crucial component of any microscopic models. Moreover, the sensitivity of layer structure to applied potential argues that the structure must be measured in the presence of the electrolyte (*in situ*) and under electrochemical control. Various optical spectroscopies have been used to probe excited vibrational and electronic states on the surface, but it is very difficult to relate these measurements uniquely to local site structures. Scanning tunneling and atomic force microscopies have been used to obtain atomic-scale "pictures" of the substrate surfaces and of the UPD layers. Such "pictures" can give a good *qualitative* idea of the basic structure (e.g., is the surface relatively ordered? do the atoms form a hexagonal net?), but cannot yield detailed information about atom positions (e.g., what is the distribution of adsorbate atom separations? what is the adsorbate-substrate atom separation?). Furthermore, the layer structure is sufficiently sensitive to applied potential that it is difficult to be confident that these probes do not disturb the surface they are measuring. Finally, although it is used widely to obtain detailed structural information about ordered surfaces, electron diffraction is not a suitable *in situ* probe of these interfaces. Low-energy electrons simply cannot penetrate to the interfacial region.

It is not surprising, therefore, that several groups have made extensive efforts to develop *in situ* x-ray probes of the structure of the electrolyte/layer/substrate interfacial region. X rays

interact much more weakly with matter than do electrons, and can therefore penetrate to the interfacial region with acceptable losses in intensity. X-ray diffraction (XRD) and x-ray absorption spectroscopy (XAS) yield largely complementary information. Using a single-crystal sample, XRD can reveal the overall two-dimensional long-range translational symmetry of the adlayer, and its angular registry with the substrate surface. It is also possible, but more difficult, to obtain the distribution of atoms within the two-dimensional unit cell, the positions of these atoms relative to the substrate atoms, and the time-averaged distributions of the atoms about the lattice sites (i.e., the direction-dependent Debye-Waller factors). None of this information can be obtained, however, if the adsorbed layer is not highly ordered at long range. XAS, on the other hand, yields detailed information about short-range structure, specifically the chemical species and numbers of the atoms neighboring the adsorbate atom and the distributions of distances to them, including substrate, electrolyte, and other adsorbate atoms. It is also possible to determine the angle between the near-neighbor atom position vectors and the surface normal \hat{n} . Moreover, XAS is *equally* able to yield this information in the presence or absence of long-range order. As will be seen, this is a crucial difference between XRD and XAS in this application.

In order to obtain a measurable signal from the UPD adlayer, XRD studies are carried out using oriented single-crystal metal substrates. To maximize the relative contribution of the UPD layer, its "in-plane" diffraction pattern is usually measured at "grazing incidence," which typically means that the incident x rays make an angle of $\sim 0.8^\circ$ with the surface of the sample. [The maximum angle for total external reflection of the x rays at the surface varies with x-ray energy and the metals involved but is typically closer to 0.6° .] The diffracted beams are measured at the same angle, so that the scattering vector parallel to \hat{n} (Q_z) is small but not zero. "In-plane" diffraction can reveal the two-dimensional translational symmetry of the UPD adlayer, its orientation relative to the underlying substrate, and occasionally some additional information like Debye-Waller factors. Measurement of the "out-of-plane" diffraction pattern (i.e., the truncation rods) as a function of Q_z can yield limited information about atomic correlations perpendicular to the interface, such as the Debye-Waller factor and the distance between the UPD adlayer and the topmost substrate layer. The diffraction due to the UPD layer is sufficiently weak that these experiments benefit greatly from using the very intense x radiation available from synchrotron radiation sources. Moreover, it is apparent from the literature that obtaining a measurable signal from the UPD adlayer requires a very high degree of translational order extending over tens of nanometers.

XAS studies can be carried out on the single-crystal samples used for XRD, but it is usually sufficient if the crystallites making up the surface are oriented with one particular axis parallel to \hat{n} . [The axes in the plane of the surface may be randomly oriented.] Even this restriction can be waived if one is content to measure an average of UPD adlayers grown on a mixture of substrate crystal faces. The simplest XAS experiment measures the transmission of a monochromatic beam through a thin uniform sample. The absorption coefficient μ is proportional to the logarithm of the ratio of the incident to the transmitted intensity. For x-ray energies immediately above the characteristic minimum energy to photoexcite an electron from a tightly bound core level to the continuum, μ is dominated by that photoexcitation process. The oscillations in μ , the x-ray absorption fine structure (XAFS), can be analyzed to yield the chemical species and numbers of the atoms near the excited atom and the distribution of their distances from it. Since the characteristic energies of different chemical species are well separated from one another, the environments of each atom species can be probed separately.

The contribution of an atom to μ as measured in transmission is proportional to its concentration in the material. For dilute samples, the ratio of signal to noise (S/N) can be increased significantly by measuring the intensity of the (fluorescent) x rays emitted when the empty core level is filled, which is proportional to the absorption coefficient of the excited atom species only. Since the energy of the fluorescent x rays is characteristic of the excited atom species, it is possible to increase S/N by discriminating against other x rays entering the detector. Moreover, in the case of UPD layers, the small number of adsorbed atoms are all at the interface between the electrolyte and the substrate. Sensitivity to those atoms can be enhanced further by orienting the substrate so that the x rays are incident at an angle somewhat below the maximum angle for total external reflection, typically $\sim 0.6^\circ$. This maximizes the x-ray electric field vector at the surface (and thereby the XAS signal from the interfacial region) while restricting the penetration of the substrate to an evanescent wave with a decay length of ~ 3 nm (and thereby minimizing the contribution of the substrate). In addition to measuring the fluorescent yield at grazing incidence to obtain the XAFS, it is also useful to measure simultaneously the specular reflectance. The reflectivity exhibits an absorption edge and oscillations related to the XAFS. Moreover, its magnitude and shape as a function of x-ray energy or angle of incidence can yield valuable information about the surface roughness, the surface density and distribution of UPD adatoms, and the thickness of the electrolyte layer.

At the angles used for these XAS experiments, the x-ray electric field at the interface is sufficiently sensitive to the angle of incidence that that angle must be controlled to within 0.1 mrad for reproducible results, requiring a similar alignment of the surface normal for all portions of the sample. Therefore, although it is theoretically possible to construct a very large substrate for XAS from metal films grown on several pieces of mica, it would be quite difficult to align them adequately. In fact, it is not routine to obtain this degree of flatness from a single crystal of mica. Of course, it is always possible to reduce this sensitivity by increasing the angle of incidence, but the cost in S/N is significant. Published XRD studies have in fact made just that choice.

The XAFS oscillations arise from atoms within ~ 0.5 nm of the excited atom, and are completely insensitive to the presence or absence of long-range order. All near atoms with a relatively sharp distribution of distances from the excited atom will contribute, including those in the electrolyte as well as substrate and adsorbate atoms. Furthermore, the photoelectron is emitted preferentially parallel to the x-ray electric field vector. If the polarized x rays from a synchrotron are used in the XAS experiment, as is usually the case, appropriate orientation of the sample will allow preferential probing of the interfacial structure either perpendicular or parallel to the surface normal. In the following discussions, these geometries are labeled s and p, respectively, in analogy with visible-light experiments.

The requirements for the electrochemical cells for *in situ* XRD and XAS studies of UPD layers are sufficiently similar that one cell can do for both. The cell must allow the electrodeposition of a UPD layer. Subsequently, it must be possible to expose the layer to grazing-incidence x radiation, and to detect the specularly reflected beam and either the diffracted beams (XRD) or the fluorescent radiation (XAS), maintaining electrochemical control at all times. This last requirement cannot be met without a *very* thin layer of electrolyte, preferably not more than ~ 10 μm . Electrodeposition of a uniform UPD adlayer over a large area would be greatly complicated if the electrolyte layer were that thin. This conflict is resolved by covering the

electrolyte with a flexible plastic sheet which facilitates maintaining a thick layer during electrodeposition and a thin layer during x-ray measurements. This arrangement has the additional benefit of allowing vertical orientation of the sample surface, useful in both XRD and XAS studies. Similar cells are used in all the measurements reported below.

Results of other research groups

Apart from an early study [1], reported XRD studies of UPD layers have been confined to a few examples of a single case, a large adatom on the smoothest surface of an fcc metal of smaller atoms: Pb/Ag(111) [2,3]; Pb/Au(111) [2]; Tl/Ag(111) [4,5]. [The relevant atomic radii are $R_{Ag}=0.145$, $R_{Au}=0.144$, $R_{Tl}=0.172$, and $R_{Pb}=0.175$ nm.] It would not be surprising to find that a complete monolayer formed a close packed (hexagonal) structure, as it would on jellium, slightly modified by the electron density in the substrate. And this is exactly what the XRD studies have found: two-dimensional hexagonal lattices with nearest neighbor distances slightly compressed from the bulk metals. Moreover, no other structure has been observed in diffraction, despite the richness of structural possibilities implied by voltammetry. Decreasing or increasing the surface coverage (short of bulk deposition) have consistently caused the diffraction pattern of the UPD adlayer to disappear.

In contrast, XAS studies have focused on the case of a small adatom (Cu) on the (100) and (111) faces of an fcc metal of a larger atom (Pt or Au) ($R_{Cu}=0.128$ and $R_{Pt}=0.139$ nm) [6-15]. Adatom size will clearly not place severe restrictions on surface site occupancy in this case, leading to the expectation of a richer set of structural possibilities. Voltammetry indicates the existence of a variety of (meta)stable coverages and structures as a function of applied potential. This expectation has been realized in the XAS measurements.

In the case of Cu/Au(111), Blum et al. [6] analyzed the Cu K-edge XAFS in p polarization and found evidence for O neighbors of Cu at ~ 0.21 nm (i.e., Cu-O pairs) but no compelling evidence for the presence of substrate atoms. In a subsequent s polarization measurement of the same system, Melroy et al. [7] deduced Cu-Au pairs at 0.258 nm (which is surprisingly short) and Cu-Cu at 0.292 nm. A later s measurement by Tajeddine et al. [8] yielded evidence for Cu-Cu at 0.289 nm but none for Au neighbors. In the case of Cu/Au(100), Tourillon et al. [9] found evidence in s polarization for Cu-O at 0.197 nm and Cu-Cu at 0.266 nm, but none for Au.

An s polarization measurement of Cu/Pt(111) by White et al. [10] yielded some evidence for Cu-Cu at 0.288 nm. In an s polarization measurement of Cu/Pt(100), Durand et al. [11] found evidence for Cu-O at 0.197 nm and Cu-Cu at 0.309 nm, but none for Pt neighbors.

2. Scientific accomplishments

Our own studies have probed the structure of Cu UPD layers on Pt [12-15]. In order to improve the low S/N which characterizes the above studies, we chose to use a very large substrate (25x250 mm) formed by vapor deposition of Pt onto a 12 mm thick bar of float glass. The resulting film is polycrystalline but predominantly (111) orientation. Given the size of the needed electrochemical cell, we were able to obtain reproducible UPD layers and stabilize them for the hours required for the x-ray measurements only after a great deal of effort. In fact, we found that only XAS data are sufficiently sensitive to structure to confirm UPD layer stability. Our use of the National Synchrotron Light Source at Brookhaven as the exclusive source of x

rays limited us to three iterations per year, substantially slowing our convergence toward a properly designed experiment. The resulting data are, however, clearly of much higher quality than those in the above studies. They cover a larger range of energy with greater S/N and are highly reproducible. We were also the first to measure a single UPD layer in both polarizations. We find O, Cu, and Pt neighbors of Cu at the same distances in both polarizations, although the amplitudes differ as expected. Combining the results for the two polarizations allows us to determine the number of neighbors and the average angle between the surface normal and the nearest neighbor vector independent of any model. Those results are summarized in the following table.

species	number ($\pm 30\%$)	distance (± 0.003 nm)	θ_n ($\pm 6^\circ$)
O	2.6	0.206	45°
Pt	5.5	0.258	48°
Cu	2.5	0.263	60°

The Cu-Cu distance is significantly less than the Pt-Pt distance in Pt metal (0.277 nm), indicating that the layer cannot be epitaxial.

The Cu-O distance of 0.206 nm is slightly longer than the Cu-O bonds in CuO or Cu₂O, or the Cu-O distance for Cu⁺⁺ in solution. The Cu-Pt distance of 0.258 nm is smaller than the sum of their metallic radii (0.267 nm). The Cu-Cu distance is 0.263 nm, significantly larger than the nearest-neighbor distance in Cu metal (0.256 nm). Finally, we found that the Cu K absorption edge energies in the two polarizations are different from one another, and that both are intermediate between Cu metal and Cu₂O. All these suggest that the Cu atoms carry a slight positive charge.

Finally, the reflectivity of the Cu monolayer has been analyzed to yield a Cu atom density on the surface of 19 at/nm² ($\pm 10\%$). This is somewhat greater than the density of atoms on the (111) surfaces of either Cu or Pt (17.7 and 15.0 at/nm², respectively). Our estimate is consistent with the determination from voltammetry and quartz microbalance work that there is approximately a single monolayer of Cu atoms on the surface, but is considerably more accurate than either.

The simplest model for a (111) monolayer of Cu would predict 6 Cu and 3 Pt nearest neighbors of each Cu atom. We find twice as much Pt and half as much Cu as that, suggesting strongly that we have intermixing of Cu and Pt atoms on the surface and a correspondingly complex structure.

Our results for UPD Cu on Pt are clearly at variance with the work of others. Those studies found no Pt and Cu at large distances only. The only point of agreement is the O distance found by Durand et al. [11], but an earlier study [10] found no evidence for O. These differences cannot be due to polarization since we measured both and found consistent results. Nor are they likely to be due to the use of single crystal substrates in the earlier studies, since our substrates included both (111) and (100) faces. It is most likely that the principal difference is in the higher quality of our data. Firstly, we transform approximately 750 eV of XAFS oscillations, while the other studies transform 350 to 450 eV. Secondly, our sample area is at least 50 times greater, and we still accumulated data for 3 to 5 hours with a very intense x-ray source. As a consequence, our S/N must be much greater. This is confirmed by the spectra shown in the first study [10]. In

other words, the other groups would need much higher quality data to make a case against our results.

Furthermore, we have found it necessary to apply stringent tests of self-consistency to our data. For example, if we grow a UPD layer with the substrate horizontal (for an s polarization measurement), we will then accumulate data for a few hours in s, a few hours in p with the substrate vertical, and then again in s. The quality of the spectrum from a single 30 min. data scan is sufficient that it is meaningful to compare the first and last scans in each set (s or p), as well as the first and last scans of the entire sequence. We are sensitive to changes as small as a few percent in coverage or structure, and can therefore confirm layer stability. Moreover, we measure the specular reflectivity during each scan, which can yield the angle of x-ray incidence, the surface density of Cu atoms, and the electrolyte layer thickness in addition to providing a spectrum related to the XAFS. We demand self-consistency of all this information before we accept the results of the XAFS data analysis. I do not believe that the other groups apply such stringent tests.

Finally, we use sophisticated XAFS data analysis techniques [16] which have been improved and refined over nearly twenty years. Most of the other XAFS studies of UPD systems make at least one crucial mistake in their analysis procedures, often a step which is flatly contrary to currently accepted practice. The most common mistake is to back-transform separately two peaks which are actually overlapping in r space. This will always yield misleading results.

It is a reasonable supposition in the absence of compelling evidence to the contrary that the structure of UPD Cu on Au will be at least similar to the structure of Cu on Pt. It is therefore of interest at this point to examine the results of the studies of UPD Cu on Au. One might expect to find O, Cu, and Au neighbors in both polarizations. Only one study found any evidence for Au [7], but they deduced an unphysically short Cu-Au distance (0.258 nm). Two studies found evidence for O neighbors [6,9], and those are at distances which are consistent with our findings. Three studies found evidence for Cu, but only one of those reported a distance consistent with metallic radii.

All in all, these studies are not consistent with each other. There are many potential reasons for this, including possible differences in the samples, but I believe there are five deficiencies in each of the reported experiments to be addressed before looking for more fundamental causes:

- 1) the data range analyzed is too short;
- 2) the ratio of signal to noise is too low;
- 3) the stability of the UPD layer is inadequately tested;
- 4) the specular reflectivity should be measured, and explained self-consistently with the XAFS data;
- 5) the data analysis practices are well below state-of-the-art, and are often inadequate.

There have been three additional XAS studies by other groups. In a p-polarization measurement of UPD Pb/Ag(111), Samant et al. [17] found evidence for O neighbors of Pb, but *neither* Pb nor Ag. A study of Ag/Au(111) in p polarization by White et al. [18] yielded O at 0.242 nm and Au at 0.275, but no Ag. Both of these distances are somewhat surprising. Later, Samant et al. [19] studied Ag on Au(111) in both s and p polarizations. Unfortunately, they used data analysis procedures which are clearly incorrect. It is therefore difficult to know what to

make of their claimed evidence for O, Ag, and Au neighbors even though the distances are much more reasonable. In fact, all three of these studies are open to the above five criticisms.

What, then, is the status of this field? X-ray diffraction has the potential to yield a great deal of significant information about UPD layers. Unfortunately, this potential has not been realized. Only one structure has been found to yield a measurable diffraction pattern: a close-packed hexagonal lattice of large adatoms on the (smooth) fcc (111) surface of smaller atoms, as found in Pb/Ag(111), Pb/Au(111), and Tl/Ag(111). While the IBM research group involved did obtain a fair amount of information on two of these systems, their work has been confined to a very small subset of the rich structural variety indicated for UPD layers. Since this same research group is also responsible for XAS studies of Cu and Ag on Au(111), it seems likely that they have attempted to carry out XRD studies of these systems as well, and failed. I conclude therefore that XRD studies are very difficult without both a high degree of long-range order and a heavy atom scatterer (having a high cross section for x rays).

XAS studies have largely been confined to another class of UPD systems, involving a small adatom on an fcc metal composed of larger atoms. XAS is the first, and still the only, technique to conclusively identify O atoms as closely bound near neighbors of the adatoms. This is a very important contribution to our understanding of UPD systems. Beyond that, however, the studies have often been poorly executed and have yielded contradictory information. Nearly all the studies have suffered from a range of data which is too short, poor S/N, too few tests for self-consistency and stability, and inadequate (and even incorrect) data analysis techniques. On the other hand, analysis of the successes and failures of these studies does yield the requirements for a proper x-ray measurement of the structure of UPD layers. The difficult ground work appears to have been largely accomplished, and the field appears ready for significant advances in our understanding of UPD layers.

3. Experimental design and technique development

Samples

We were convinced from the very outset of this research program that advances in our understanding of electrochemical interfaces would come only from much higher quality data than that which had been obtained in earlier studies. We decided accordingly to increase the ratio of signal to noise substantially by adopting a very large polycrystalline Pt substrate. The high quality of the data obtained with these substrates greatly facilitated a number of important experimental design changes, as detailed below. With our present understanding of the requirements of this experiment, it would now be appropriate to switch to a single crystal surface providing it were not too small.

Our Pt substrates were 100 nm films evaporated onto 25×250 mm float-glass bars which were 12 mm thick. Optical interferometry showed that these bars have less than 200 nm of long-range deviation from perfect flatness. The Pt films were grown at the Stanford Synchrotron Radiation Laboratory in their large evaporation system designed to fabricate x-ray mirrors. The Pt film was bound to the glass with 20 nm of Cr.

We characterized the Pt films with x-ray diffraction, finding a preference for (111) orientation (approximately half of the area of the sample). The rest of the surface was equally shared by

grains with (100) and (110) orientations. While the polycrystalline character of our substrates is a complication when it comes to detailed modeling of the surface structure, it does help us avoid the complication of Bragg diffraction from the substrate.

Sample chamber and mounting stage

The Pt-coated glass bars were mounted in a Teflon sample chamber which was fitted with a double Kapton top window. The double window arrangement was intended to preclude the diffusion of oxygen through the Kapton. The second window was ~3 mm above the primary window, and oxygen-free nitrogen was continuously passed through the region between the windows. This is important since our results confirm that Cu is highly coordinated with oxygen. Other investigators have detected oxygen neighbors, but have often attributed their presence to oxygen diffusion through the Kapton.

The primary window was sealed with a Viton O-ring. This seal turned out to be the biggest sample cell problem during the course of the project. The thickness of the water layer could be controlled only if we could control the pressure in the cell and the tension in the window. Many of these difficulties were connected to the large sample size and its rectangular shape. We built several sample chambers of different materials. We always returned to Teflon because of its superior chemical resistance. Its tendency to flow under pressure, however, made it difficult to establish adequate seals. Our typical failure mode would be under slight negative pressure, where air would leak into the electrolyte chamber in the form of a slowly growing bubble. Our best data were obtained under conditions where the leak was extremely small or absent.

The sample chamber was mounted on a tilt-translation stage for control of the incident angle. The latter was remotely operated by a portable computer. The two degrees of freedom made it possible to rotate the sample about its center with better than 0.2 mrad accuracy. The ion chamber was held at a fixed position above the sample. The entire assembly could be rotated, however, about an axis along the incident x-ray beam to allow changing between s- and p-polarization without removing the electrochemical control. In addition to the large sample, this aspect of our experimental design was unique among electrochemical XAFS efforts.

Polarization combination

We were the first to measure the XAS spectra from a single layer with both s- and p-polarization. This is very important since it is possible to combine the data from both polarizations to obtain a model-independent measure of both the coordination number and the average angle between surface normal and near neighbor vector for a particular neighbor.

Electrochemical control

Electrochemical control was established with wire electrodes that entered the sample chamber through gas-tight seals. The counter electrode was a Pt wire coil and the reference electrode was a pure Cu wire. The latter established an exchange reaction with the Cu ions in solution, thus defining a reversible condition. This technique has the advantage of providing a positive identification of the Cu plating voltage. We were very careful to avoid bulk Cu deposition and its possible restructuring influence on the first layers. It is also known that Cu can diffuse into Pt under multilayer deposition.

The electrolyte, which was externally purged with oxygen-free nitrogen, was introduced into the sample chamber by means of a liquid delivery system. The latter was also used to control the pressure in the chamber. With a slight positive pressure, excess liquid forced the Kapton window away from the sample. This facilitated electrochemical control and was the condition under which all Cu deposition and stripping were conducted. With a slight negative pressure, the Kapton window was pressed against the sample, trapping a thin layer of electrolyte against the metal. Under this condition we could still control the surface by the conductivity made possible by an acid electrolyte. The electrolyte layer was sufficiently thin to enable the x rays to reach the sample with significant intensity even at grazing incidence.

The electrochemical control electronics followed conventional practice. We chose compact units that could be easily transported, but these same instruments were heavily used at CSM for testing and improvement of the sample control practice.

Our long sample geometry enabled us to establish reproducible positioning in the x-ray beam. The method was based on use of a narrow slit after the sample, which allowed only the unreflected beam to pass through to the subsequent detector. With this setup, we could move and rock the sample until it was accurately parallel to the beam.

X-ray detectors

Our main detector for this experiment was a specially built ionization chamber matched to the size and shape of our sample. We also built two Söller slits of Ta foil, one for each polarization configuration. The detector contained five metal-wire electrodes. These were biased using a battery. An integrated pre-amplifier was built into the detector. The entire assembly was housed in lead sheet to eliminate spurious radiation. The performance of this detector was outstanding. Its dark noise was very low and, when filled with argon or an argon/quench-gas mixture, it provided adequate sensitivity and dynamic range for our needs.

An energy-dispersive intrinsic-Ge detector was used to characterize both the incident radiation at the synchrotron beam line and the fluorescence from the sample. Both roles provided important information for our experimental design. We did not use this detector, however, to accumulate XAS data. Its inability to handle high count rates would have led to much lower S/N than our ionization chamber, even taking advantage of its energy dispersive ability.

X-ray spectroscopy

Three detectors are used in the standard fluorescence-detection XAFS experiment, to measure incident, fluorescent, and transmitted (or, in our case, reflected) flux. We added a fourth detector after the third and placed a thin Cu foil between them. We could then measure the Cu metal XAS spectrum simultaneously with monolayer reflectivity and fluorescence, providing a continual calibration for the energy of the incident x rays. We found, as is commonly the case, that loose mechanical linkages in the x-ray monochromator led to as much as a 3 eV shift in the apparent x-ray energies.

We established the means to perform an abbreviated data analysis sequence using computer equipment which we brought to the synchrotron each time we ran the experiment. Although a full analysis of the data took several man-months to complete for each run, this on-site capability enabled us to evaluate and modify our experiment during the course of the week. This was an

important advance, since many subtleties of the data can be appreciated only after Fourier transformation of the results of multiple scans.

X-ray reflectivity

We have established a detailed model for the x-ray reflectivity of the electrolyte/Cu ML/Pt interfacial region. The reflectivity depends strongly on several parameters of our system, including the water layer thickness, surface roughness, and the density of Cu atoms on the substrate. A model for the reflectivity was constructed based on the Fresnel coefficients. Subsequent non-linear optimization of the parameters of this model to fit the measured reflectivity yielded values for the water thickness (~ 13 μm), the surface roughness (~ 1.5 nm), and the copper area coverage (~ 19 at/nm²). We also discovered that the predicted variations in reflectivity as a function of energy imply a significant modification of the amplitude of the XAFS. We are the only group to have incorporated this effect into our data analysis. Finally, analysis of the x-ray reflectivity during the experiment allowed us to set the angular orientation of the sample to within 0.1 mrad and to respond to variations in water layer thickness. This proved to be crucial feedback.

Cu and electrolyte layer stabilities

We have verified that the water layer thickness can be kept constant during the 10 hours necessary to complete a series of measurements. Our awareness of this issue and our ability to monitor water layer thickness contribute significantly to the overall quality of our data.

We have verified that the Cu layer can also be kept constant under electrochemical control. We occasionally observed spectral changes due to changes in the thickness of the water layer (when pressure control was lost) or changes in the background concentration of Cu ions. The latter was an undesirable side effect of the Cu-wire reference electrode. This problem was avoided by reducing the exposed area of this electrode to a minimum, so as to reduce the total amount of dissolving Cu.

Ni filter artifacts

In analyses of early data, we found a long-period oscillation which simulated a neighbor at a very small distance from Cu. Our data were sufficiently noise free that we could examine the XAFS to unusually large k values, where the extra oscillations were particularly prominent. We identified the source of this effect only recently. In our experiment, the Compton scattered x rays passing through the Ni filter before our ionization detector were contributing Ni XAFS to the spectrum. The unanticipated feature of these oscillations is that they grow stronger as the energy increases, not weaker. This was particularly prominent in our s-polarized data, where Compton scattering is higher in intensity. By correctly understanding this effect we were able to remove its influence from the data. This eliminated a spurious neighbor from our spectra and brought the s- and p-polarized spectra into excellent agreement. Moreover, data taken over a three-year period are internally consistent when these systematic effects are taken into account.

Sample oscillator

In order to analyze XAFS data accurately, it is essential to calibrate the analysis procedure using measured spectra from materials of known structure, referred to typically as "standards." An important standard in this experiment is an alloy of $\sim 1\%$ Cu in Pt, used to determine the

number and position of Pt atoms about Cu atoms in the UPD layer. In our first attempt to measure the XAS spectrum of this material, we rolled the alloy to an appropriate thickness and performed a transmission experiment. The resulting spectrum was sufficiently distorted by diffraction features to be useless. It is known that the grains in FCC metals tend to orient upon rolling and also that the XAS spectra of single-crystal samples can be made useless by large diffraction features, but the effect is surprisingly strong in this case. Notably, the deleterious effect of diffraction features has been an important unsolved problem in XAS for some time. We decided to address this directly by building a holder which can oscillate a sample by a few degrees about two axes perpendicular to the incident beam during the measurement. The efficacy of this procedure has been demonstrated in application to single-crystal semiconductors [20]. It was used to generate the spectrum needed for this experiment.

X-ray optics

It became clear early in this research program that the macroscopic metrics traditionally applied to determine the state of a UPD layer are inadequate. Only XAS spectra are sufficiently sensitive to be useful. At this time, however, only the x rays from synchrotron sources are intense enough to yield useful XAS spectra. In order to provide an eventual solution to this problem, we undertook to develop the capability to measure at least the x-ray absorption near edge spectra of UPD layers in our laboratory at RPI. In addition to purchasing an intense rotating-anode x-ray generator, we pushed the state-of-the-art in concentrating x radiation. We designed and built a variable-radius bent-crystal monochromator, which will provide a ten-fold increase in flux with the necessary energy tunability for XAS studies. We also investigated the use of promising wide-band-pass x-ray lenses constructed from small-diameter glass capillaries [21-23]. This research is ongoing.

Technique summary

This program has played a dominant role in the development of electrochemical XAS as a valuable tool for the study of buried interfaces. We achieved the highest ratio of signal-to-noise for a system of this type. This enabled us to eliminate experimental artifacts which are usually hidden in electrochemical XAS spectra. As a result, we developed several procedures which are necessary to reach high precision. Our prototype system, Cu on Pt, proved to be more complicated than we had anticipated. Our data are of such high quality, however, that we can adopt a "blind perspective" regarding their interpretation. Our experiment has resolved troubling inconsistencies found in earlier studies of this specific system. In addition, we have demonstrated that XAS can be successfully applied to study electrochemical phenomena and have established a standard of quality for subsequent projects of this type.

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5. Personnel

This seven-year research program has been a collaboration between two groups, led by T M Hayes and T E Furtak. It began while we were both at the Colorado School of Mines (CSM), funded under ONR grant N00014-87-K-0551. Two years into the work, I moved to Rensselaer Polytechnic Institute (RPI). The renewal was therefore funded as two ONR grants: N00014-90-J-1332 with T M Hayes as principal investigator at RPI; N00014-90-J-1326 with T E Furtak as principal investigator at CSM.

The basic division of responsibilities was that Hayes at RPI took responsibility for the x-ray portions of the research, including experimental design and data analysis, while Furtak at CSM took responsibility for the electrochemistry. The work reported herein resulted from that collaboration, although the results obtained at RPI are emphasized.

The personnel at RPI included the following:

- a. Postdoctoral fellows
 - Gan Liang (October 1989 - August 1990)
 - Jayashree Pant (January 1991 - September 1993)
 - Laurence Lurio (September 1992 - May 1994)
- b. Graduate students
 - Weidan Li (September 1989 - August 1990)
 - Lih-Wen Hwang (September 1989 - December 1989)
 - Gay Kendall (January 1990 - May 1990)
 - Chun Ming Lo (January 1990 - May 1990)
 - Jifang Zhang (September 1991 - May 1992)
 - Valerie Iskandarian (July 1992 - March 1993)
 - Jeffrey Marx (January 1993 - August 1993)
 - Robert Olsson (January 1993 - May 1994)
- c. Undergraduate students
 - Karl Pansewicz (June 1991 - May 1992)
 - Markian Petrina (September 1992 - December 1992)
 - Alan Catelli (January 1993-June 1993)
 - Bishan He (June 1993-August 1993)
 - Brian Standley (January 1993 - December 1993)

6. National facility use

The x-ray experiments were conducted at national synchrotron radiation laboratories at Stanford University and Brookhaven National Laboratory through competitive awards of general user time. Our proposals received high ratings, enabling us to run once per scheduling period. Between trips to the synchrotron the CSM group was involved with sample handling, chamber improvement, electrochemical testing, and other auxiliary experiments designed to help in the interpretation of the x-ray results. The RPI group carried out analysis of the data and made x-ray experimental design improvements. Over the course of the project we made eleven trips to national facilities. Each experimental run consisted of four to six days of 24 hr time as a general user. At NSLS we worked at beamline X9, which was built and is operated by the National Biostructures Research Resource.

7. Publications

- T M Hayes, W Li, G Liang, C M Lo, T E Furtak, E A Creek, P Samanta, and L Wang, "Underpotential-deposited Cu monolayer on Pt", in *X-ray Absorption Fine Structure*, ed by S S Hasnain (Ellis Norwood, New York, 1991) 229-231
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- J Pant and T M Hayes, "New technique to enable measurement of the x-ray absorption spectra of single crystals," *Rev Sci Inst* (in press)
- L B Lurio, J Pant, T M Hayes, L Wang, and T E Furtak, "XAS study of the liquid/UPD Cu/Pt interfacial region," *Physica B* (in preparation)
- L B Lurio, J Pant, and T M Hayes, "Amplitude correction for fluorescence-detection surface XAS experiments," *Physica B* (in preparation)
- J Pant, J Zhang, T M Hayes, L Wang, and T E Furtak, "Identification of stable state of underpotential-deposited Cu on Pt" (in preparation)
- 14 presentations at international technical meetings and symposia